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RESEARCH ARTICLE - BASED ON MIR INVESTIGATIONS IN LAKE GENEVA

Spatial heterogeneity of benthic methane dynamics in the subaquatic canyons of the Rhone River Delta (Lake Geneva)

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Abstract Heterogeneous benthic methane (CH_4) dynamics from river deltas with important organic matter accumulation have been recently reported in various aquatic and marine environments. The spatial heterogeneity of dissolved CH_4 concentrations and associated production and diffusion rates were investigated in the Rhone River Delta of Lake Geneva (Switzerland/France) using sediment cores taken as part of the éLEMO Project. Benthic CH_4 dynamics within the complex subaquatic canyon structure of the Rhone Delta were compared (1) between three canyons of different sedimentation regimes, (2) along a longitudinal transect of the 'active' canyon most influenced by the Rhone River, and (3) laterally across a canyon. Results indicated higher CH_4 diffusion and production rates in the 'active' compared to the other canyons, explained by more allochthonous carbon deposition. Within the active canyon, the highest diffusion and production rates were found at intermediate sites further along the canyon. Stronger resuspension of sediments directly in front of the river inflow was likely the cause for the variable emission rates found there. Evidence also suggests more CH_4 production occurs on the levees (shoulders) of canyons due to preferred sedimentation in those locations. Our results from the heterogeneous Rhone delta in Lake Geneva further support the concept that high sedimentary CH_4 concentrations should be expected in depositional environments with high inputs of allochthonous organic carbon.

Keywords Porewater · Diffusion · Sedimentation · Organic matter · Particle size · Methane emission · Methane production

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Introduction

Atmospheric methane (CH_4) concentration has dramatically increased since the pre-industrialized era to reach

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levels of 1.75 ppm (Reay 2010). This greenhouse gas has a high global warming potential (Forster et al. 2007) and is currently under intense investigation in various environments. Many aquatic systems act as CH_4 sources, thereby counter-balancing a portion of the terrestrial carbon sink (Bastviken et al. 2011). Although great efforts are being made to constrain these emission rates, the contribution of CH_4 emitted from freshwater lakes is difficult to estimate due to the temporal and spatial variability of methane production, transport and emission.

Methanogenic bacteria produce CH_4 from the degradation of organic matter in anoxic aquatic sediments, which are typically depleted in alternate electron acceptors such as nitrate or sulfate (Martens and Berner 1974; Schulz and Conrad 1995; Segers 1998). CH_4 production has long since been identified as one of the most important processes of organic matter degradation in aquatic sediments (Schulz and Conrad 1995). It therefore makes sense that organic carbon inputs stimulate methanogenesis in surface sediments (Segers 1998). However, the quality of detritus has also been identified as an important factor accounting for the variability in CH_4 production and emission in certain environments. CH_4 diffusion at the sediment–water interface has been found to be higher when the CH_4 originates from fresh, labile and easily degradable organic material (Segers 1998; Kankaala et al. 2003). CH_4 dynamics in such environments also include processes that inhibit CH_4 production and provoke CH_4 oxidation by oxygenating the surface sediments, either by the gas transport itself aerating the sediments (Segers 1998) or the resuspension of sediment exposing CH_4 to more oxygen (Bussmann 2005).

Much of the work on the impact of terrestrial loading or local vegetation on CH_4 production and emission has been reported for wetlands (e.g., Christensen 2004). However, less attention has been paid to CH_4 dynamics in similar environments found in lakes, particularly large lakes. One of the first comprehensive studies of CH_4 emissions from lakes found correlations with more general lake characteristics such as surface area (Bastviken 2004), although most of the lakes analyzed were quite small (<1 km^2). Gas emissions from large lakes, however, are characterized by significant spatial heterogeneity that precludes a correlation with lake size, particularly if the lake receives significant loading from inflowing rivers. For example, CH_4 emission hotspots have been found in lacustrine littoral zones (Murase et al. 2005; Hofmann et al. 2010) and in river deltas of a large reservoir (DelSontro et al. 2011), both of which are often associated with high organic matter accumulation.

River deltas, in particular, are subject to high organic loading and are typically very dynamic, encountering rapid changes in loading and accumulation of allochthonous material (e.g., during flood events) (Boldrin et al. 2005). High CH_4 concentrations in the sediments of the Po Delta in the Mediterranean Sea, for example, are attributed to the fast burial of terrestrial material (Furlanetto et al. 2012). In Lake Constance, located in central Europe, CH_4 emissions are highest in the old Rhine River Delta where biogenic CH_4 bubble emissions, in particular, are associated with distinct geomorphic structures such as pockmarks (Wessels et al. 2010; Bussmann et al. 2011). Finally, large spatial heterogeneity of CH_4 emission has recently been observed in a large tropical reservoir where emissions from small river deltas were orders of magnitude higher than emissions from littoral bays with no river input, also mostly due to bubble emissions (DelSontro et al. 2011). Thus, river deltas are ideal locations for potential CH_4 emission hotspots.

The goal of this study was therefore to relate sediment dissolved CH_4 concentrations, as well as CH_4 diffusion and production rates, to the complex structure of subaquatic canyons found in the Rhone River Delta of Lake Geneva and the carbon deposition pattern to which they are linked (Sastre et al. 2010). The present work was part of the larger éLEMO project that examined several chemical, physical, biological and geological characteristics of the lake (this issue). Of particular interest to our study are the sediment deposition processes in the Rhone delta, which are well detailed in Corella et al. (2013), and discusses the interplay between erosion and sedimentation along the main canyon (henceforth called the 'active' canyon) extending from the river flow. We measured sediment dissolved CH_4 concentrations along transects in three of the subaquatic canyons of the delta and estimated production and diffusion rates in each. We also used particle size and the organic carbon-to-organic nitrogen (C:N) ratio of organic matter in sediments to identify the origin of the organic substrate most likely used for CH_4 production (i.e., whether it was terrestrial or aquatic). According to delta geomorphology and bathymetry, we hypothesized that CH_4 production in and emission from delta sediments should (1) be highest in the active canyon and lower in canyons no longer heavily impacted by the Rhone River; (2) decrease in the active canyon with increasing distance from the river mouth due to diminishing sedimentation of allochthonous organic matter; and (3) be higher at depositional sites laterally across a canyon, such as canyon levees (shoulders), and lower at erosional sites, such as canyon floors. We conclude with a discussion of the fate of CH_4 in this complex system and how anthropogenic impacts may have altered the CH_4 dynamics in the delta.

Methods

Study site

Lake Geneva is the largest western European lake with a surface area of 582 km^2, a volume of 89 km^3, and a maximum depth of 309 m. The lake has a residence time of ~12 years and is almost always thermally stratified (Michalski and Lemmin 1995). The Rhone River, with a catchment area of 5,220 km^2, brings about 68 % of the total water discharge (Burkard 1984), which originates from industrial and urban sites, agricultural lands (16 %), pastures and forests (46 %), and glaciated areas (38 %) (Haubert et al. 1975; Monna et al. 1999). High Rhone River discharge occurs from May until October when Alpine melting stops, until the high-altitude catchments start freezing again. The Rhone River inflow is characterized typically as an 'interflow,' in which the colder, sediment-laden river water intrudes into the thermocline. Summer flood events, however, are common and turbid 'underflow' currents will follow the slope of the delta due to the extra density of suspended particles from the catchment (Lambert and Giovanoli 1988). The discharge has been heavily modified over the last half century due to upstream construction of hydroelectric dams, which reduce summer flows and increase winter flows (Loizeau and Dominik 2000). As a result, flood events decreased in number and sediment storage increased in the upstream reservoirs.

At the Rhone River inflow into Lake Geneva, this dynamic river system has led to a complex underwater structure composed of nine underwater canyons, each with a different origin based on the various inflows to the lake throughout its history. Sastre et al. (2010) described the evolution of the Rhone delta based on historical maps, as well as geologic and bathymetric data, concluding that three different river mouths coming from the Rhone River were present until the mid-1,800 s and caused the erosion that formed the canyons. Eventually the Rhone River was reduced from three branches to one, which is now the only location of its influence in the delta and predominantly affects the active canyon (Girardclos et al. 2012). During flood events, two overflow canyons to the east of the main channel can be temporarily activated but most of the other canyons do not receive any loads from the Rhone at present (Sastre et al. 2010; Corella et al. 2013). The Rhone delta is approximately 100 km^2 (Houbolt and Jonker 1968) and is shown in full extent in Fig. 1.

Sampling

In this study, three of the nine canyons were investigated (Fig. 1) according to their ages and historical evolution: (1) the active canyon ('*C8*' in Sastre et al. 2010), which receives continuous input from the Rhone River and extends ca. 10 km from the river mouth to the deep basin of the lake, was sampled along a longitudinal gradient from the delta to the deep basin; (2) a more central canyon (hereafter called 'central canyon'; '*C5*' in Sastre et al. 2010), which receives main Rhone River loads only during flood events but is constantly supplied by the Vieux Rhone with a moderate discharge, was sampled laterally across the canyon to produce a cross-sectional profile; and (3) a canyon located further east (hereafter called 'eastern canyon'; '*C3*' in Sastre et al. 2010) that no longer receives any inputs from the main river, was sampled for comparison with the other two canyons. Twelve sediment cores were taken from a boat with a modified UWITEC gravity corer. Eight cores were taken from MIR submersibles, equipped with robotic arms, using the 'éLEMO corer' described in Girardclos et al. (2012).

In the active canyon, a longitudinal coring transect divided the canyon into three regions of which cores from the two further offshore regions were taken along the northern levee (shoulder of the northern canyon wall; Fig. 1). The three surveyed regions were (1) a shallow proximal region consisting of sites A1, A2, and A3 (22–50 m depth); (2) the northern levee in an intermediate region consisting of sites A4, A5, and A6 (82–118 m depth); and (3) the distal northern levee consisting of sites A7 and A8 (209–220 m depth).

MIR submersibles were used to locate precise coring sites across the canyon/levee complex in the central canyon (C1–5, 59–78 m depth). This cross-sectional transect was sampled to understand whether local morphology has an influence on CH_4 production and emission of a single canyon that may display an 'average' sedimentation regime compared to the active and eastern canyons (Fig. 1). Additional cores from a research vessel were retrieved in shallower areas of this canyon (C6 and C7, 35–40 m depth).

In the eastern canyon, a total of five sites were cored (E1–5, 50–93 m depth) in specific mount-like structures and levees using the éLEMO corer from the MIR submersible and from a research vessel. Altogether, a total of 20 coring sites in all three canyons allowed the comparison between the canyons.

At each location, two cores were taken—one for CH_4 measurements and one for geochemistry analyses and sediment characteristics. A list of all core sites and the material analyzed is shown in the supplementary material (Table S1 and S2 in the supplemental material, SM). Sediment dissolved CH_4 concentrations were measured by collecting porewater and sediment from holes pre-drilled into core liners (resolution: 1 cm). Approximately 2 ml of sediment was extracted and added to glass bottles (20 ml) pre-filled with NaOH (30 %, 4 ml), as described in Sobek

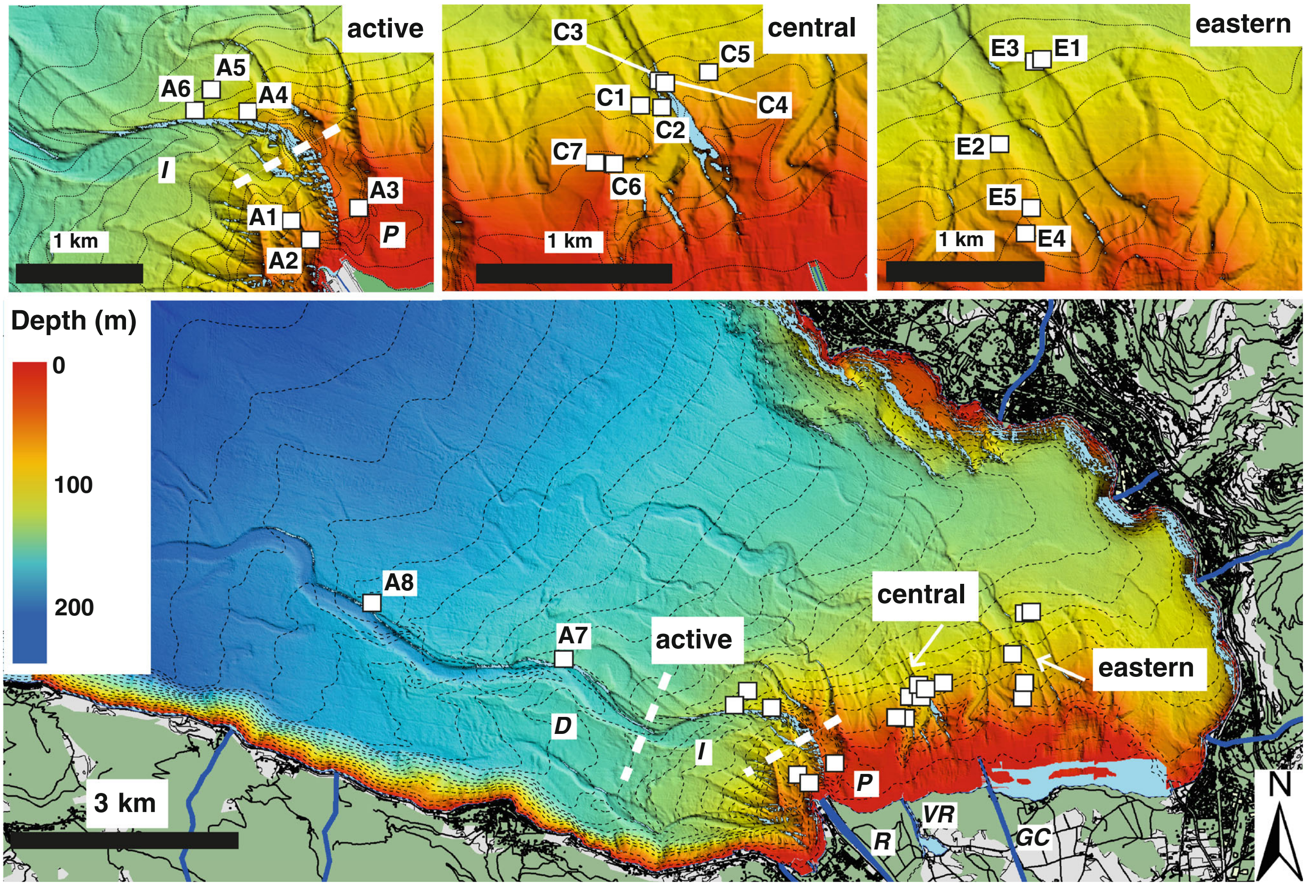

Fig. 1 Shaded relief map of active, central and eastern canyons of the Rhone delta in Lake Geneva (map adapted from Sastre et al. 2010 in which canyons are named C8, C5, and C3, respectively). Sampling locations are labeled A1–8 in active canyon, C1–7 in central, and E1–5 in eastern. *Top panel* maps show sampling locations in detail. The full extent of the delta ($\sim$100 km^2) is shown in the bottom map. The active canyon is subdivided into a proximal (*P*), intermediate (*I*), and distal (*D*) regions by *thick dashed lines*. *Thin*, *black dashed lines* represent isobaths with a resolution of 10 m. The main inflows to Lake Geneva are shown: Rhone (*R*), the Vieux Rhone (*VR*), and the Grand Canal (*GC*)

et al. (2009). Assuming equilibrium between the water and headspace after some time, CH_4 was measured via a gas chromatograph equipped with a flame ion detector and porewater concentrations were back-calculated using Henry's Law. To compare observed concentrations with saturation concentrations of CH_4, we used the temperature and water depth at each coring site and a modified Henry's equation for solubility (King 1969; Schmid et al. 2003).

The other core taken at each site were split in half lengthwise, subsampled with a resolution between 1 and 5 cm, and freeze dried to calculate water content and for performing the following analyses: typical resolutions for total nitrogen (TN) and total organic carbon (TOC), porosity (ϕ) and grain size were between 1 and 4 cm for the top 10 cm, whereas resolution decreased to between 3 and 10 cm for the remainder of the core. In the active canyon, a lower resolution was chosen for the grain size due to the length of those cores ($\geq$34 cm). TN and TOC were measured using an Elemental Analyzer. Grain size was measured on a laser particle analyzer (Malvern Mastersizer 2000, Limnogeology Laboratory, ETH Zurich, Switzerland) where the fractions of clay (0.01–2 µm), silt (2–63 µm) and sand (63–2,000 µm) were determined. Density (ρ) was measured at 5-mm resolution via a Geotek multi-sensor core logger (MSCL) at the Limnogeology Laboratory (ETH Zurich). Porosity (ϕ) was calculated according to Berner (1982) using measured water content and density.

Methane areal production rates over the full core length ($R_{(z)}$; as listed in Table 1) were estimated using Fick's 2nd Law and the measured CH_4 porewater profiles, assuming steady state:

$$R_{(z)} = -D\frac{\partial^2 CH_4}{\partial z^2} \cdot z$$

where D is the diffusion coefficient for CH_4 in sediment porewater (9.2×10^{-6} cm^2 s^{-1}; Furrer and Wehrli 1996), CH_4 signifies concentration and z, the depth. For more details, see the extended methods section in the SM.

Table 1 Areal production ($R_{(z)}$) and diffusion (J) rates calculated within the entire core length (depth) and the top 4 cm, respectively

Cores	$R_{(z)}$ (mg CH_4 m^{-2} day^{-1})	Depth (cm)	J (mg CH_4 m^{-2} day^{-1})
Active canyon (region)[a]			
A1 (*P*)	61	49	0.3
A2 (*P*)	−11	66	−1.1
A3 (*P*)	51	27	29
A4 (*I*)	[c]	44	37
A5 (*I*)	56	20	31
A6 (*I*)	203	26	16
A7 (*D*)	15[b]	10	16[b]
A8 (*D*)	−191	19	4.0
Mean	26		16.5
Central canyon			
C1	−29	8	3.7
C2	109	17	11
C3	−35	6	15
C4	−68	20	6.6
C5	−5.5	12	11
C6	20	39	5.1
C7	28	39	9.0
Mean	−16		8.7
Eastern canyon			
E1	12	13	8.0
E2	−8.1	21	2.1
E3	−7.8	69	3.2
E4	5.3	69	3.5
E5	15	69	4.9
Mean	2.3		3.3

Negative $R_{(z)}$ values indicate consumption but in this study it may be more due to short core lengths not reaching the production layer

[a] *P*, *I* and *D* stand for proximal, intermediate and distal regions of the active canyon. Locations can be found on Fig. 1

[b] Diffusion and areal production rates are considered similar so that all CH_4 produced in A7 reached the sediment–water-interface

[c] Not at steady state

Diffusion from the sediments was calculated according to Fick's 1st Law using the top 4 cm of the measured CH_4 gradient and the empirical equation from Maerki et al. (2004) to correct for the effects of porosity and tortuosity on diffusion in sediments:

$$J_s = -\frac{D}{F} \cdot \frac{\partial CH_4}{\partial z}$$

where F is a formation factor of a porous media that varies according to the sediment type and porosity ($F = 1.02 \times \phi^{-1.81}$ or $1.04 \times \phi^{-1.21}$ for clay-silt and sandy sediments, respectively).

Results

'Active-inactive' canyon comparison

Sedimentary facies in the active canyon are described in detail in Corella et al. (2013), but in short they consist of alternating hemipelagic sediments and turbidites. Turbidites are flood layers consisting of sand to silt layers with a fining upward texture capped on top by a thin clay sublayer and are often quite enriched in terrestrial organic matter. Hemipelagic sedimentation consists of triplets of calcite layers, organic debris layers containing allochthonous and autochthonous material, and detrital layers of mostly terrestrial origin that was transported from the river and dispersed as interflow. Sediment cores in the central and eastern canyon show this hemipelagic sedimentation as well, but are lacking turbidites (data not shown).

The grain size data indicate that silt was dominant in the delta of Lake Geneva comprising between 69 and 90 % of the sediments (Fig. 2a; Table S2 in SM). A substantially higher fraction of sandy sediments was found in the active canyon (28.7 %) compared to the central (6.1 %) and eastern ones (3.2 %). In contrast, clays were more abundant in sediments further away from the Rhone River mouth (i.e., to the east; Fig. 2a). Porosity of the sediments followed expected trends with the more sandy sediments in the active canyon being less porous than the finer-grained sediments of the central and active canyons (Fig. 3b). In general, relatively low organic carbon concentrations were observed in the sediments of the delta with slightly higher amounts in the central and eastern canyons (median 0.64 %) than in the active (0.59 %) canyon; although maximum values were highest at the Rhone inflow with 1.8 % compared to 1.0 % in the central and eastern canyons (Fig. 2b; Table S2). Slightly higher C:N ratios were also measured in the active canyon of the Rhone delta with a median value of 14.7. In the same region, more than 10 samples with C:N ratios above 25 were observed, whereas such high values were absent in the central canyon and far less present in the eastern canyon (Fig. 2b).

Dissolved CH_4 concentrations in the porewater varied between canyons and sampling sites (Fig. 3; Fig. S1 in SM). Levee sites (A6, C4 and E5) were chosen for a direct comparison of porewater CH_4 between the three different canyons (Fig. 3a) as they represent areas of continuous sedimentation (Corella et al. 2013). The active canyon clearly has higher and slightly more variable concentrations, while the eastern canyon has low and constant values. The central canyon levee profile is more similar to the active levee with a steep gradient at the top, but maximum concentrations are reached deeper in the core. The CH_4

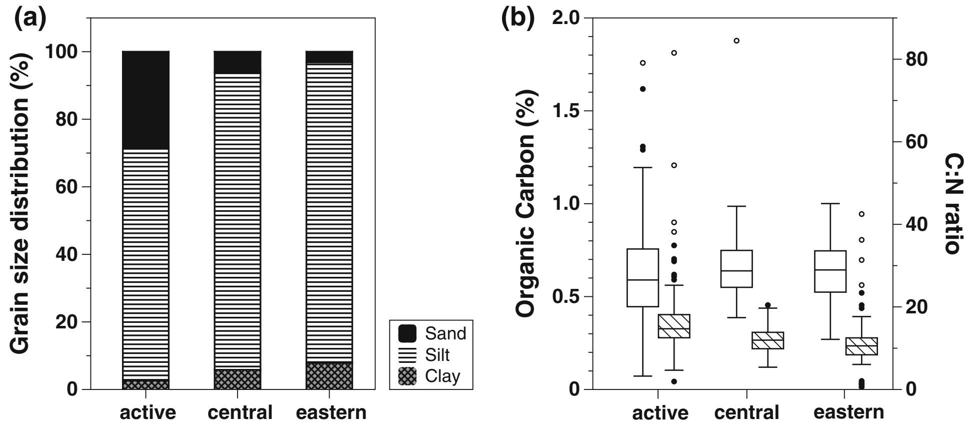

Fig. 2 Sediment geochemistry of the upper 31 cm of each core from the active, central and eastern canyons. **a** Average grain size distribution per canyon where the number of samples (n) for the active, central and eastern canyon are n = 15, 26, and 41, respectively. **b** *Empty boxplots* are of total organic carbon content of all core samples in the active (n = 120), central (n = 83) and eastern (n = 46) canyons. *Hashed boxplots* are of C:N ratios of all samples from all cores per canyon and correspond to the right axis. *Boxplots* show 50 % of the values within the *box* with the median represented as a line in the middle. Whiskers contain 90 % of the values and dots are outliers. Values also found in Table S2

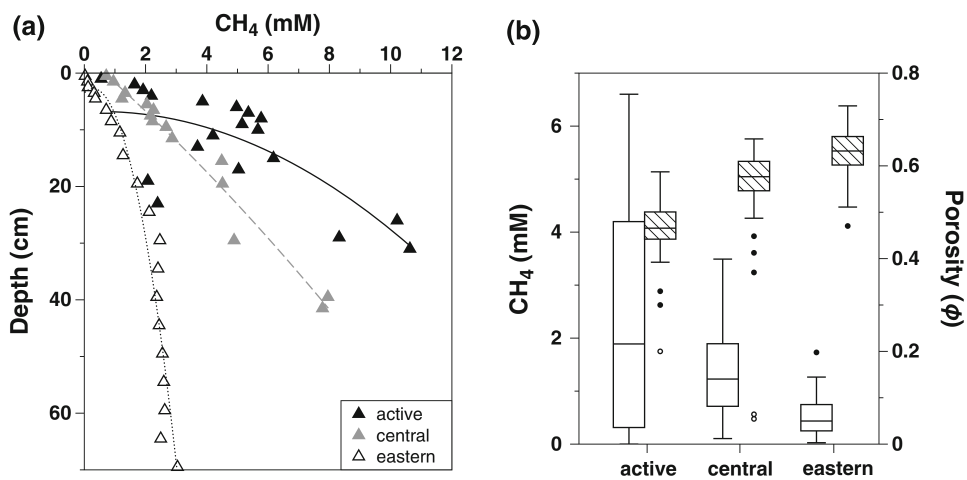

Fig. 3 **a** Porewater CH_4 profiles on proximal levee sites A6, C4, and E5 in the active, central and eastern canyons, respectively (see Fig. 1 for locations). Fitted functions are 2nd order polynomial lines with correlation coefficients (R^2) of 0.55, 0.97 and 0.92 for the active, central and eastern canyons, respectively. **b** *Empty boxplots* show variability of dissolved CH_4 for each cm of the top 10 cm of each core in the active (n = 75), central (n = 69) and eastern (n = 44) canyons, where 50 % of the observations are contained within the boxes and the whiskers contain 90 % of the values. *Line* in the *box* and *dots* outside the box show the median and outlier values for each canyon, respectively. *Hashed boxplots* are of porosity per canyon and correspond to the right axis (values found in Table S2)

concentration gradient in the porewater of the active canyon levee, where the Rhone River enters, was by far the steepest, reaching maximum concentrations above 20 cm depth. Comparing just the top 10 cm of all cores (i.e., depths most important for diffusive emissions), we find that porewater in the active canyon contained higher amounts of dissolved CH_4 (median 1.9 mM) than in the central (1.2 mM) and eastern (0.4 mM) canyons (Fig. 3b; Table S2). However, dissolved CH_4 concentration in the sediment was more variable in the active canyon, ranging from 1.2×10^{-3} to 6.6 mM, compared to the central (0.1–3.5 mM) and eastern canyons (2.7×10^{-2} to 1.7 mM).

Estimated CH_4 production rates, $R_{(z)}$ (Table 1), showed more positive values (i.e. production rather than consumption) in the active canyon with 71 % (average, $\sim$26 mg CH_4 m^{-2} day^{-1}) of the coring sites being production layers in comparison to the eastern (60 %, $\sim$2.3 mg CH_4 m^{-2} day^{-1}) and central canyons (43 %, approximately -16 mg CH_4 m^{-2} day^{-1}). Negative values indicate CH_4 consumption within the sampled core length, which occurred in the majority of the central cores (4 of 7 cores) in comparison to the active (2 of 7 cores) and eastern canyons (2 of 5 cores). Diffusive CH_4 fluxes were calculated from the porewater CH_4 gradients and indicated that fluxes (Table 1) were more intense in the active canyon (16.5 ± 14.7 mg CH_4 m^{-2} day^{-1}, average ± standard deviation) than in the central and eastern regions (8.7 ± 3.8 and 4.4 ± 2.3 mg m^{-2} day^{-1}, respectively).

Active canyon longitudinal study

The longitudinal survey of the active canyon consisted of three regions that were investigated (proximal sites A1–3, intermediate sites A4–6, and distal sites A7–8; Fig. 1). Silt made up only 57 % of the proximal canyon sediments, followed closely by sand (41 %; Fig. 4a). The fraction of sand decreases with increasing distance from the river mouth with 22 and 20 % in the intermediate and distal regions of the active canyon, respectively. A clear transition from a lower to a higher organic content offshore was measured, although values were still quite low (median range 0.3–0.74 %; Fig. 4b; Table S2 in SM). There was substantial variability in carbon content in the proximal region but it decreased slightly along the canyon. While the median C:N ratios were quite constant among the three domains (range 14.6–15.8; Fig. 4b; Table S2), the variability decreased with distance from the river mouth.

Sediment profiles of dissolved CH_4 concentrations in active canyon cores revealed different dynamics in the three longitudinal sections (see examples in Fig. 5a). Concentrations at site A1 in the proximal region were low (<1.5 mM) for the first 15 cm, and reached a maximum value of 6 mM at 34 cm depth. In contrast, CH_4 increased linearly in the first centimeters at A4 in the intermediate region and the maximum concentration was observed just below 10 cm (12.6 mM). Concentrations varied widely within a 6 mM range for the rest of the profile. Similarly to the proximal core, CH_4 concentrations at site A8 in the distal region were very low until 15 cm sediment depth where they started to increase with depth. The median value of CH_4 was the highest in the intermediate region (2.7 mM), but also highly variable with concentrations ranging from 0.1 to 6.6 mM (Fig. 5b; Table S2). The proximal region exhibited the lowest CH_4 values (median 1.2×10^{-3} mM), while in the distal region moderate values were found (1.2 mM).

The highest production rates were found in the intermediate region with lower values in the proximal region and even lower rates in the distal region (Table 1). Diffusion rates were slightly higher in the intermediate region.

Canyon cross-section study

The underwater canyons are delimited by walls with often quite steep slopes (45–50° in the active canyon; Girardclos et al. 2012). The central canyon has a wall on either side but also has a middle ridge that subdivides the canyon into two channels (Fig. 1). Sediment cores and corresponding porewater CH_4 profiles taken across this canyon reveal some interesting trends (Fig. 6). The CH_4 gradients of cores C1–5 were very similar for the first 10 cm, albeit concentrations were higher in C4, which was the levee core. The canyon floor core (C2) was one of the longest cores taken with maximum CH_4 values (5.1 mM) found at 11 cm of the 17 cm long core. The C4 levee core, on the other hand, had the highest CH_4 concentrations observed in the cross-section with maximum values (8.0 mM) located at the bottom of the 20 cm long core. The highest CH_4 production rate was found in the canyon floor (109 mg CH_4 m^{-2} day^{-1}, C2 core), whereas in all other core locations

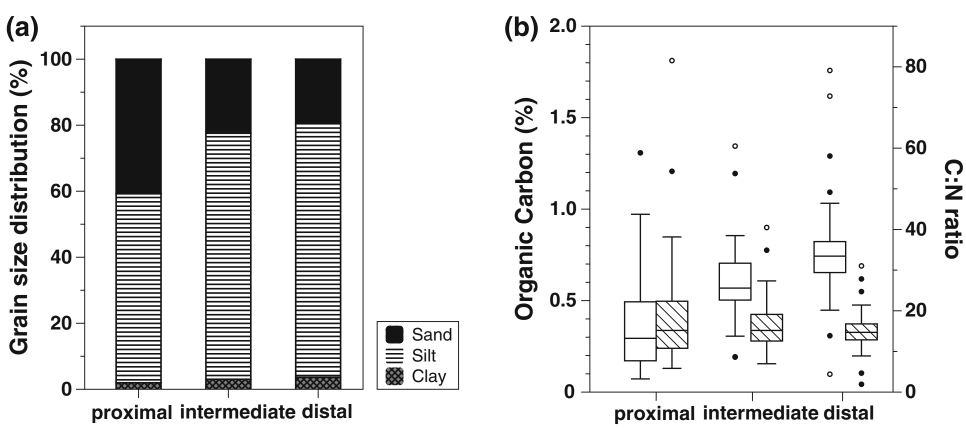

Fig. 4 Sediment geochemistry of the upper 34 cm of each core in the proximal, intermediate and distal regions of the active canyon. **a** Average grain size distribution per region (proximal, n = 8; intermediate, n = 23; distal, n = 41). b) *Empty boxplots* are of organic carbon content of all samples per region (proximal, n = 55; intermediate, n = 44; distal, n = 31). *Hashed boxplots* are of C:N ratios of all samples per region and correspond to the right axis. *Boxplots* show 50 % of the values within the *box* with the median represented as a *line* in the middle. Whiskers contain 90 % of the values and *dots* are outliers. Grain size % and median values of organic carbon and C:N are also presented in Table S2

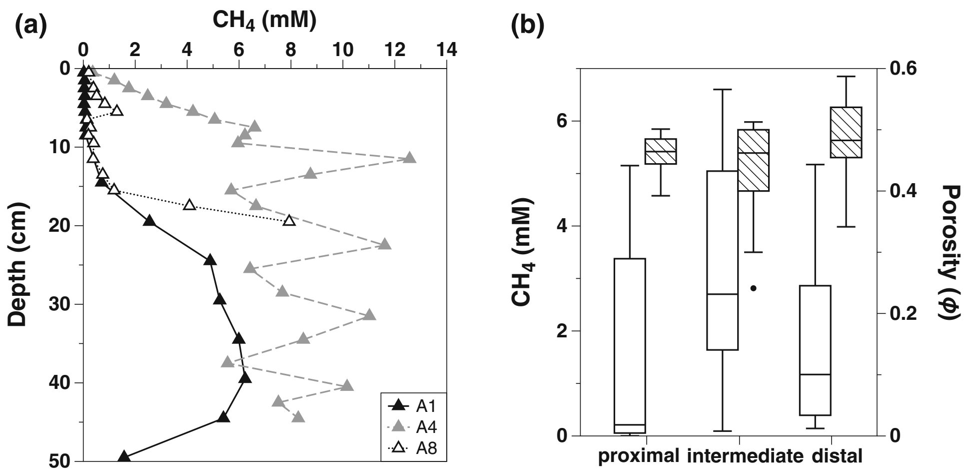

Fig. 5 **a** Comparison of porewater CH_4 sites A1, A4 and A8 in the proximal, intermediate and distal regions, respectively (see Fig. 1 for locations). **b** Variability of dissolved CH_4 concentrations (normalized to only the upper 10 cm of each core) in all cores per region of the active canyon (proximal, n = 25; intermediate, n = 30; distal, n = 20) illustrated by *empty boxplots*, where 50 % of the observations are contained within the *boxes* and the whiskers contain 90 % of the values. *Line* in the *box* and *dots* outside the box show the median and outlier values for each canyon, respectively. *Hashed boxplots* are of porosity per region and correspond to the right axis (values found in Table S2)

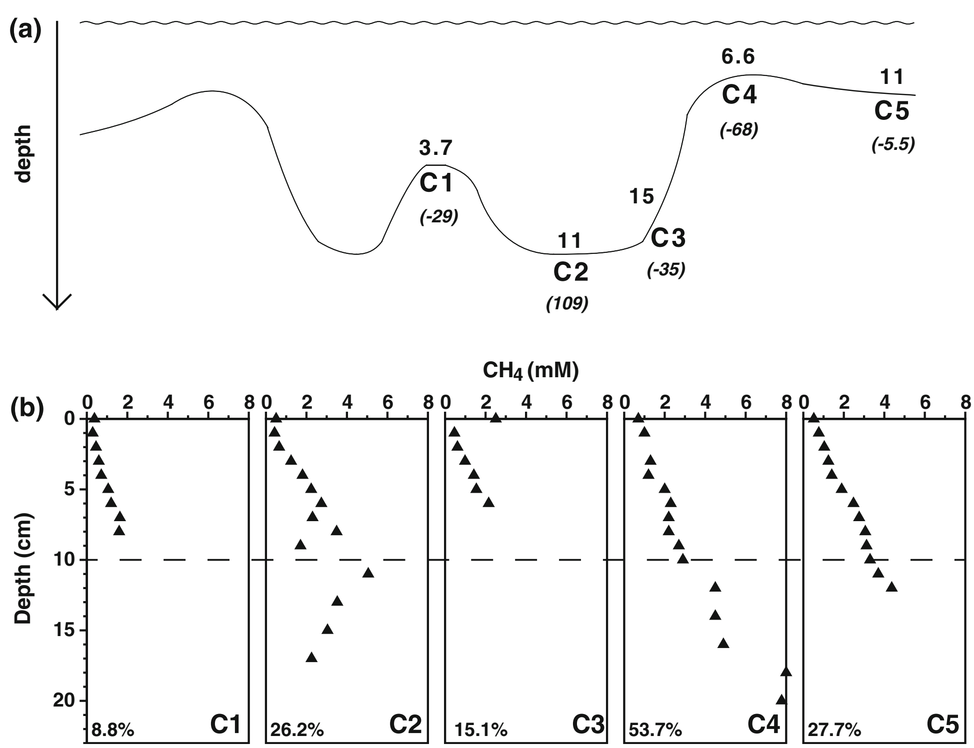

Fig. 6 **a** Schematic view of the central canyon cross-section with specific sites labeled (C1, center ridge; C2, canyon floor; C3, base of the wall; C4, levee; and C5, off-levee). Figure not to scale. Numbers above schematic are calculated diffusion rates and below in parentheses are areal production rates ($R_{(z)}$). Both values given in mg CH_4 m^{-2} day^{-1}. **b** CH_4 profiles and percentage of CH_4 saturation reached for corresponding sites

consumption may have occurred. The highest consumption rate was found on top of the levee (C4 core). At the sediment–water interface, CH_4 diffusion rates were highest at C3, the base of the wall site (15 mg CH_4 m^{-2} day^{-1}), but in general diffusion rates were of the same order of magnitude (8.7 ± 4.3 mg CH_4 m^{-2} day^{-1}). The lowest CH_4 concentrations and diffusion rates were found on the center ridge, which has the lowest concentration gradient.

Discussion

The CH_4 cores taken, especially by the MIR submersibles, were typically no more than 30 cm in length. According to Corella et al. (2013) and Loizeau et al. (2012), the sedimentation rate in the Rhone delta fluctuates from >3 cm $years^{-1}$ in the proximal active canyon to <0.5 cm $years^{-1}$ in the easternmost area of the delta.

Therefore, most of the sediment cores, particularly the shorter ones, document only the last 20–30 years of sediment accumulation. In the following, we confine our discussion to the factors governing CH_4 concentrations and dynamics in different subaquatic canyons of the Rhone Delta taking into account the short sedimentation history that most of our cores represent.

The varying CH_4 dynamics of the Rhone delta canyons

Our first hypothesis that CH_4 production and emissions would decrease with distance from the river mouth (i.e., from active to central to eastern canyon) was mostly correct. Higher dissolved porewater CH_4 and subsequent production and diffusion rates were measured in the active canyon, where the Rhone River directly enters the lake, as opposed to the other canyons. Porewater CH_4 concentrations in the central canyon were more similar to the active canyon than the eastern one, which had substantially lower CH_4 levels. Similar results were obtained from estimating production rates in each canyon, although the amplitude of the difference between the three canyons is much smaller. The highest production rates were located in the active canyon, but higher values were found in the eastern canyon compared to the central one. The rates estimated in the central canyon, however, may not be entirely accurate as the limitation when estimating production rates is that the core length must resolve the production layer. The average core length in the active (33 cm) and eastern (37 cm) canyons was much higher than that in the central canyon (20 cm). It is more likely that the production layer was reached at the longer core locations, especially in this particular delta environment where sedimentation rate is relatively high in general (2.6 cm years^{-1} in comparison to 1.9 and 0.8 cm years^{-1} in the central and eastern canyons, respectively; Loizeau et al. 1997, 2012; Corella et al. 2013). As the accuracy of the production rates was limited by the fact that the short cores may have sampled only a portion of the production layer, the apparent low production rates in the central canyon may therefore be due to a sampling bias introduced by the short core lengths.

Higher C:N ratios indicate more of a terrestrial organic matter input (Meyers and Ishiwatari 1993). Thus, while organic matter concentrations were similar in all canyons, the C:N ratio indicated more allochthonous (i.e., terrestrial) input into the active and central canyons than into the eastern one. This was expected for the active canyon as it is heavily influenced by the Rhone River discharge, as also evidenced by the large amount of sandy sediments there. The central canyon may also experience loading from the Rhone during flood events as highlighted by Sastre et al. (2010), but these authors also stated that this region still receives some loading from the Vieux Rhone. The lower C:N ratios in the eastern canyon suggest a higher input of autochthonous organic matter there than in the canyons closer to the river mouth. A likely explanation for this C:N ratio gradient is the sediment dynamics of the Rhone Delta. Large terrestrial loads can be transported through the active canyon by underflows caused by floods and mass movements as evidenced by turbidites (Lambert and Giovanoli 1988; Girardclos et al. 2012; Kremer et al. 2012). At times, these loads can transport material eastward, but allochthonous material is more frequently supplied by common interflow processes, which supposedly cover a large area (Girardclos et al. 2012). However, our data suggest that the eastern canyon remains quite isolated from the interflows initiated by the Rhone River inflow.

According to our second hypothesis, we expected to see decreasing CH_4 concentrations and fluxes from the river mouth to the distal sections of the active canyon. Interestingly, however, porewater CH_4 concentrations were close to zero in the top 15 cm of the proximal cores (sites A1 and A2), which resulted in quite low diffusion rates. Higher CH_4 concentrations were found at site A3 but this core was taken in a different location further northeast of the two other sites in the proximal region. Production rates were also quite variable in the proximal delta cores as a result of the variability in concentrations. Ultimately, the intermediate region of the delta contained the highest diffusion and production rates of the canyon, while the sediments of the distal region of the active canyon contained the highest organic carbon.

The CH_4 dynamics in the active canyon can primarily be explained by the sediment and hydrodynamic processes that the canyon is subjected to by the Rhone River. The proximal sediments exhibited a higher sand fraction and lower cohesiveness compared to the other sites and are in the region most heavily influenced by underflows (Lambert and Giovanoli 1988; Loizeau 1991) and localized erosion and deposition (Girardclos et al. 2012). The Rhone River's strong bottom currents may cause resuspension and the observed depletion of CH_4 in the upper sediment layers, either via aeration and subsequent oxidation of the sediments or the initiation of some mechanical release of the CH_4 (Bussmann 2005; Hofmann et al. 2010). In the most shallow regions, the low CH_4 concentrations could also be linked to dredging by the local gravel company (Sastre et al. 2010). Organic carbon deposited in this region also may not be efficiently buried due to resuspension from the constant reworking by the river currents (Girardclos et al. 2012; Corella et al. 2013), at least not in the surface sediments directly in front of the river inflow. However, at the shallowest sites in the proximal delta, two cores were at or close to CH_4 saturation. The proximal region is likely an environment conducive for ebullition, which was visibly observed during surveys.

The intermediate region of the active canyon was characterized by the presence of more frequent, thicker and coarser turbidites than in the other regions (Corella et al. 2013). These authors emphasized that the highest concentrations of CH_4 in one of the intermediate levee cores was contained within a thick, sandy turbidite layer deposited during underflows. The fine clay layer lying above the sandy turbidite displayed higher shear strength with less effective porosity (Corella et al. 2013). This fine top layer could act as a seal allowing the accumulation of higher CH_4 concentration within the sandy intervals below. The higher fraction of sandy sediments in the intermediate cores in comparison to the distal ones further supports the hypothesis of a greater probability for such a sealing to occur. The highest CH_4 concentrations of the entire survey were found in a turbidite layer in an intermediate levee site, A4 ($\sim$12 mM; Fig. S1), which showed active degassing via observed bubble formation when the core was opened in the laboratory (Fig. S2 in SM). The highly variable, zigzag shape of this CH_4 profile highlights the dynamics in CH_4 production in this region, and most likely also reflects the variability in sedimentation and frequency of turbidites in this particular region. Ultimately, the capacity of turbidites to accumulate high CH_4 concentrations was more commonly found in the intermediate region than in the other regions.

To further explore the idea that more carbon is transported to and buried in the intermediate region of the canyon, we estimated the total organic loading from the Rhone River in the proximal and intermediate regions of the active canyon using river discharge and TOC measurements (see SM for more details). Based on Loizeau and Dominik (2000) and Burrus et al. (1989), the 2011 sediment loading was estimated with a threshold of 150 $m^3\ s^{-1}$, representing the summer–winter transition. Using the average organic carbon percentage of only the top centimeter from proximal and intermediate cores, we found that a higher amount of TOC was delivered to the intermediate region (1.3×10^5 t $years^{-1}$) than to the proximal region (0.7×10^5 t $years^{-1}$).

The highest concentration of organic carbon was found in distal canyon sediments; although this carbon was more autochthonous than that in the other regions. The distal sediments also exhibited the finest grain size in the active canyon and exhibited less erosional impact from the Rhone River as well as a lack of turbidites. The increasing organic carbon levels towards the distal region are explained by a combination of more uniform deposition patterns associated with the river inflow and an increase in autochthonous matter towards open water. Particle loads from the river settle according to size with the largest particles depositing first and the finer fractions being transported and deposited further offshore. Lower turbidity offshore will facilitate increased primary production, which will contribute to increased autochthonous organic matter accumulation in the sediments. In fact, the river should have so little influence on sedimentation at this distance that carbon burial could be higher due to less sediment reworking.

We conclude that the higher CH_4 diffusion and production rates in the active and central canyons are mostly related to terrestrial organic matter loading, as has been shown elsewhere (Furlanetto et al. 2012). In addition, CH_4 production and emission will also depend on sedimentation rate, but only if the particle load includes organic material and not just minerals. The most intense sediment accumulation in the whole delta was observed in the proximal active canyon ($>$ 2.6 cm $years^{-1}$ in proximal areas; Corella et al. 2013), where we found the highest but most variable CH_4 concentrations of all the regions. The sedimentation rate decreased towards the canyons further from the river mouth just as CH_4 concentrations, diffusion and production rates did (1–1.5 and 0.5–1 cm $years^{-1}$ in central and eastern canyons, respectively (Loizeau et al. 1997, 2012). Ultimately, we found more CH_4 produced in sediments and subsequently released into the water column in higher organic matter deposition environments like the intermediate region of the active canyon, but also in the entire active canyon in comparison to the other canyons that have slightly less organic-rich sediment and less allochthonous input. The differences between canyons highlight the large-scale spatial variability in the Rhone Delta, which is governed by sedimentation dynamics, and the budgets of suspended and organic matter.

In a third and final step, we evaluated the local variability across a single canyon to address the question whether high depositional areas such as the levees of a canyon exhibit higher CH_4 concentrations and emission. We expected some significant differences in CH_4 dynamics across the canyon as the sedimentation dynamics also vary across a canyon (Corella et al. 2013); however, the top 10 cm (equivalent to the last 10–15 years of sedimentation) of the CH_4 depth profiles were surprisingly uniform across the central canyon. Historical data show that the last extreme flood event (i.e., discharge much higher than the typical maximum of $\sim$400 $m^3\ s^{-1}$; Loizeau and Dominik 2000) occurred in the year 2000 when a maximum discharge of 1,370 $m^3\ s^{-1}$ was measured in La Porte du Scex, a hydrological station close to the river mouth (Corella et al. 2013). Most likely discharge events within the typical range (200–300 $m^3\ s^{-1}$; Loizeau and Dominik 2000) would not cause substantial erosion or impact sedimentation rates heavily, particularly away from the active canyon. Hydrological records indicate that no major flood occurred over the last decade, which corresponds well with the uniform porewater profiles in the top layers of the central canyon. Furthermore, the sediment records of these central canyon cores are characterized by a lack of turbidites, which were found to contain the highest CH_4 concentrations in active canyon cores. However, as the cores taken in this canyon were some of the shortest, CH_4 production in deeper layers might have been missed, which precludes a more conclusive test of our third hypothesis.

Impact of damming on sedimentation and methane emissions

Massive dam impoundment in the Alpine region since the 1950 s has reduced sediment loads to large peri-alpine lakes, such as Lake Brienz (Anselmetti et al. 2007; Finger et al. 2007) and Lake Geneva (Loizeau and Dominik 2000), by approximately half. Thus, together with minerogenic particles, particulate organic carbon has been trapped in upstream reservoirs (Cole et al. 2007) and does not contribute as significantly to the sedimentation regime of the Rhone River delta and its canyons. In addition to their particle retaining role (Anselmetti et al. 2007; Thevenon et al. 2013), alpine reservoirs have dramatically changed the seasonality of the annual discharge (Loizeau and Dominik 2000) with lower discharge during summer, higher discharge during winter, and a reduction of peak flood events (Finger et al. 2007). The active canyon is likely heavily impacted by such sediment and hydrodynamic regime changes. The central canyon may also feel the impact of the upstream damming as it receives significant loads from the river, but only during extreme flood events. Loading and erosion to the eastern canyon from the Rhone River ended when the section of river (or a branch of it) was disconnected from that part of the lake (Sastre et al. 2010), i.e., before the onset of hydroelectric dam construction (1950 s). A quantitative study of the impact of damming on the Rhone delta CH_4 emissions would be useful when determining the natural role that the delta and the entire lake plays in the carbon cycle of the region.

Fate of CH_4 in the Rhone Delta

Before discussing the ultimate fate of CH_4 produced in the Rhone Delta, it is useful to know whether the observed amount of CH_4 emission is even possible based on the organic carbon input. Potential total CH_4 diffusion from the sediments of the active canyon (3.0 and 8.3 t C-CH_4 years^{-1} for the 0.87 km^2 proximal and the and 0.81 km^2 intermediate regions, respectively) accounts for only a mere fraction (almost negligible) of the TOC currently entering the delta from the Rhone River ($\sim 2.0 \times 10^4$ t TOC years^{-1}; see SM for details). Diffusion of dissolved CH_4 is only a minor process in regards to the carbon cycle in this very dynamic region of the delta where deposition and erosion play major roles. The remaining TOC input was likely either buried long-term, as indicated by organic carbon measurements in the cores or, if remineralized to CH_4, lost by other processes, such oxidation near the sediment–water interface or ebullitive release (Bastviken 2004). The oxygen penetration depth measured in the active canyon was 2 mm (data not shown), which suggests CH_4 consumption occurred within the upper few mm of sediment. While these oxidation rates were not directly measured, the consequence of this process was accounted for in our diffusion estimates because the CH_4 profiles from which the estimates were based were measured at a 1 cm resolution; therefore the top centimeter sediment sample was actually an integrated view of those top 10 mm, including the 2 mm of oxic sediment. In fact, any relevant processes occurring in the sediment, such as CH_4 production, were also accounted for in the diffusion estimate as the CH_4 profile reflects the results of these processes up to the point in which the core was taken.

The amount of CH_4 released via ebullition has not been quantified in this study, but may also account for a portion of the TOC input. Bubbles were detected in the delta, particularly in the proximal region of the active canyon, and will be discussed in another manuscript as it could act as an efficient mechanism for the direct transport of CH_4 to the atmosphere from the shallower waters (<50 m) of the Rhone delta (e.g., Ostrovsky et al. 2008; DelSontro et al. 2011). Ebullition was also observed at greater depths (>80 m), but these bubbles will most likely dissolve before reaching the atmosphere (McGinnis et al. 2006). Finally, as the overlaying water column is fully oxic (Fig. S3 in ESM), any CH_4 that escapes oxidation in the sediment and enters the water column either by diffusive transport or dissolution of rising bubbles has the strong likelihood of being oxidized somewhere in the water column of the lake.

Ebullition, while not quantified in this study, is important to discuss because it is a transport process that can severely impact the fate of CH_4 in a lake. Ebullition was observed at several of our coring locations but supersaturation of CH_4, which is needed for bubble formation (Boudreau et al. 2005), was not reached in most of the cores we sampled. Although this undersaturation could be explained by artifacts of our sampling procedure that may have disrupted the uppermost sediment layers and led to degassing throughout some of the core, we propose another explanation. Only the longest cores collected displayed CH_4 levels close to saturation and those cores were taken mostly from levees (C4 in Fig. 6 and some active canyon cores). This suggests the presence of deep CH_4-saturated layers from which bubbles originate and that were not reached within most of our cores. Corella et al. (2013) observed that turbidite layers are likely locations for CH_4 saturation and bubble production and were rarely seen in the shorter ($\sim$20 cm) cores. Turbidites were found mostly in the active canyon and on levees, which are areas of high sedimentation. Thus, we speculate that levees are potential areas of elevated CH_4 emissions in the Rhone Delta and directly related to the presence of the river and where allochthonous organic sedimentation occurs. In addition, levees are also potential sites for mass-movement events, as these events are sometimes induced by high amounts of dissolved porewater gas (Lambert and Giovanoli 1988; Corella et al. 2013). Therefore, the remineralization of organic carbon is not only important in regards to greenhouse gas emissions, but also in terms of sediment dynamics. Overall, CH_4 plays a diverse role in the Rhone River Delta, but much more work is needed to constrain its ultimate fate and impact on carbon cycling in this region.

Conclusion

The significant differences between CH_4 production in and diffusion rates from the underwater canyons of the Rhone delta highlight the spatial heterogeneity of CH_4 dynamics of this particular region and, perhaps, of deltas in general. While the Rhone Delta may be a relatively unique lake delta due to its vast subaquatic canyons, deltas typically are complex environments with variable hydrology and sedimentation regimes. Therefore, CH_4 emissions from deltas cannot be adequately assessed without taking its spatial variability into account. In the same respect, deltaic regions should be considered as potential CH_4 emission hotspots when surveying gas emissions from marine and lacustrine basins in order not to underestimate gross CH_4 release from a water body. This study and a few others have shown that regions with high sedimentation rates of allochthonous organic material in river deltas are hot spots of methanogenesis. In the particular case of the Rhone Delta, historical changes of the river location, as well as upstream damming operations, led to extreme CH_4 production variability that further complicates CH_4 dynamics in this system. Ultimately though, the idea that deltaic regions are CH_4 hotspots is not only important for determining the CH_4 balance of an individual system, but also for accurately assessing global greenhouse gas budgets and the complete role that inland waters play in the global carbon cycle.

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